ISSN 0840-8440

PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE 1988

November 28 and 29, 1988

Royal York Hotel

Toronto, Ontario

SESSION D

ANALYTICAL METHODS

Sponsored by

Research and Technology Branch

Environment Ontario

Ontario, Canada

AASG

Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact ServiceOntario Publications at copyright@ontario.ca

D7

SYNTHESIS AND USE OF LIQUID CRYSTALLINE POLYSILOXANE SUBSTRATE IN CAPILLARY COLUMN GC-MS FOR ISOMER SPECIFIC SEPARATION OF TOXIC ISOMERS OF PCDD AND PCDF.

K. P. Naikwadi* and F. W. Karasek,
Department of Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1.

ABSTRACT:

The synthesis and characterization of a variety of mesomorphic (liquid crystalline) side chain polysiloxane substrate known to be useful as gas chromatographic stationary phases , are described and discussed. The synthetic scheme is based upon the hydrosilation reaction that occurs when precursor liquid crystalline alkene compounds are contacted with polymethylhydrosilane in the presence of a platinum catalyst. Liquid crystalline polysiloxane offer unique selectivity when used as stationary phase in capillary gas chromatography. Separation on such column occurred based on the size and shape of the solute molecules. Separation and quantitation of the most toxic isomers of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) generally requires the use of long polar capillary columns, that are inadequate for analysis of total PCDD, PCDF. However, the liquid crystalline polysiloxane capillary column shows unique selectivity for separation of 2,3,7,8-TCDD and TCDF, and analysis of total PCDD and PCDF in same GC-MS run can be carried out. The advantages of the liquid crystalline polysiloxane capillary column over conventional capillary columns used in analysis of PCDD and PCDF will be discussed.

Introduction:

Isomer-specific separation of polycyclic aromatic hydrocarbons (1), polychlorinated biphenyls (PCBs) and insect sex pheromones (2,3) have been reported using low molecular weight liquid crystalline stationary phases in gas chromatography (GC). Most recently , liquid crystalline polymers (LCPs) have been developed to use as stationary phases in GC and supercritical chromatography (SFC)(4-9). There are several advantages of LCP stationary phases over low molecular weight liquid crystals. The distinct advantage of thermal stability and uniform thin film formation brought in by their polymeric nature has provided the high efficiency sorely lacking in the monomeric liquid crystals.

There are two types of LCPs, main chain LCPs, that contains liquid crystalline rigid core connected by flexible spacers, and side chain LCPs, containing liquid crystalline moieties connected to the main chain as pendent groups. So far, only side chain LCPs have been used in GC and SFC. Synthesis and use of a series of liquid crystal polyacrylates in GC and SFC for isomer specific separation has been reported (4-7). Most recently developed liquid crystalline polysiloxanes (LCPSs) have shown great promises for separation of polycyclic aromatic hydrocarbons (10-12), sulphur compounds (13), and PCDD/PCDF (14). Thermal stability and efficiency of LCPS columns has been reported to be comparable to that of conventional capillary columns. In addition, LCPSs show high isomer specific selectivity for various classes of environmental pollutants.

In this paper synthesis of a series of LCPSs has been reported. A method to develop efficient capillary columns using LCPSs is described. The results of separation of environmental samples and standards on a conventional column (DB-5) and on a column developed in this study are demonstrated.

Experimental:

All chemicals were purchased from Aldrich. The PCDD standard was synthesised in our laboratory. Fly ash sample extract was obtained by soxhlet extraction of Ontario fly ash. The chemical structures of all new monomers and polysiloxanes synthesised were determined by NMR spectral analysis. General reaction scheme is shown in Figure 1.

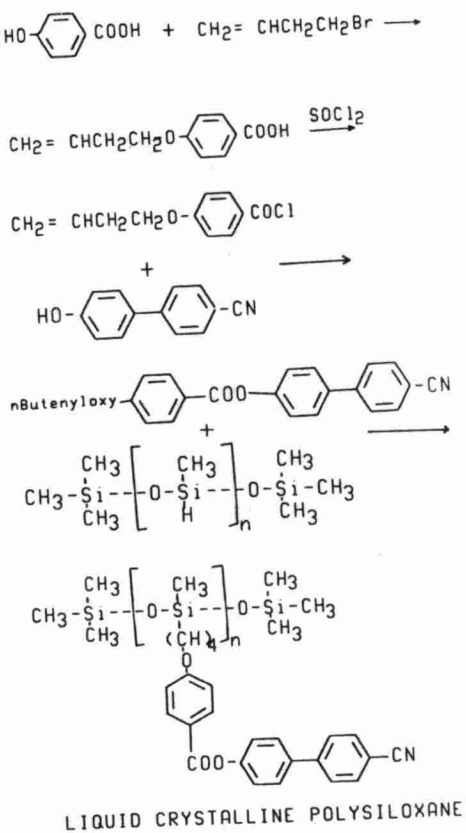


FIGURE 1. REACTION SCHEME FOR SYNTHESIS OF LCPSs

Synthesis of Liquid Crystalline Polysiloxanes:

A representative procedure for synthesis of butenyloxy benzoic acid , its chloride, alkene monomer and polysiloxane are describe below.

4-Butenyloxy benzoic acid:

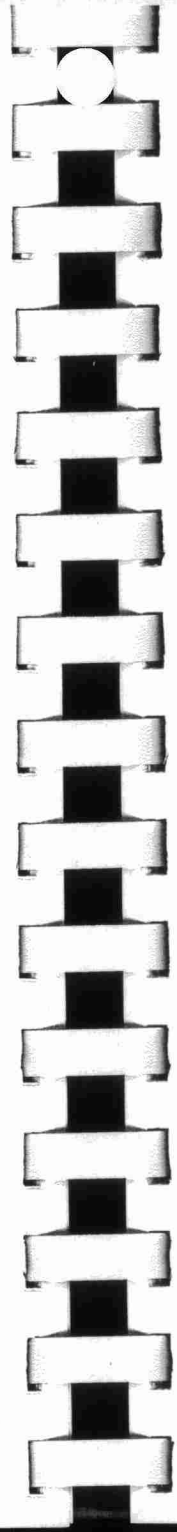
Potassium hydroxide 12.32 g (0.22 mol) was dissolved in ethanol water mixture (300:100). 4-Hydroxy benzoic acid (13.8 g, 0.1 mol) was added to potassium hydroxide solution. Potassium iodide (0.1 g) was added and mixture was heated to reflux temperature. 4-Bromo-1-butene (14.8 g, 0.11 mol) was added and the mixture was refluxed overnight. Ethanol (150 mL) was removed by distillation and the residual reaction mixture was cooled and then acidified using concentrated hydrochloric acid. The solid carboxylic acid was removed by filtration and washed with water. The air dried crude acid was recrystallised from ethanol to give 10.2 g of plates.

General procedure for esterification to form monomeric liquid crystals:

An alkenyloxy carboxylic acid was reacted at room temperature with an excess thionyl chloride containing a drop of dimethyl formamide to obtained a clear solution. The mixture was then heated to 50 ^{0}C for 2 h. and excess thionyl chloride removed by vacuum distillation. The acid chloride was dissolved in 15 mL of dry pyridine and equimolar p-substituted hydroxy benzene or biphenylene in 15 mL of pyridine was added. This mixture was heated to 100 ^{0}C for 6 h., cooled to room temperature and then added to ice water, the solid separated out was filtered, air dried, and recrystallised in a suitable solvent.

General procedure for synthesis of Liquid Crystalline Polysiloxane:

Equimolar Polymethylhydrosiloxane (PMHS, Fluka-U.S.A., Mol Wt. 2262) and liquid crystalline alkene were dissolved in 20 mL toluene. This solution was bubbled by argon for 30 min. at 80 ^{0}C. The hexa-chloro platinic acid (200ug) was added and the test tube capped and heated for 20 h. at 80 C. The reaction mixture was cooled to room temperature and then added to 100 mL methanol. The solid separated was filtered and redissolved in dichloromethane and precipitated in methanol. This process was repeated for five times. The LCPS thus obtained was dried in air and then under vacuum for 12 h. Using above procedures following monomeric liquid crystals were synthesised.



1. nButenyloxy—C(=O)—O—C$_6$H$_4$—C$_6$H$_4$—OCH$_3$

2. nButenyloxy—C(=O)—O—C$_6$H$_4$—C$_6$H$_4$—CN

3. nButenyloxy—C$_6$H$_4$—C(=O)—O—C$_6$H$_4$—OCH$_3$

4. nButenyloxy—C$_6$H$_4$—C(=O)—O—C$_6$H$_4$—CN

5. nButenyloxy-C$_6$H$_4$—COO—C$_6$H$_4$—OCH$_3$

6. $CH_2=CH-CH_2-O-$C$_6$H$_3$(OCH$_3$)—OOC—C$_6$H$_4$—C_2H_5

LIQUID CRYSTALLINE MONOMERS

Column preparation:

Fused silica capillary tubing (20 m X 0.320 mm I. D., Polymicro Technologies, Phoenix, AZ, U.S.A.) was washed by passing 10 ml methanol then purged by helium at 100 ^{0}C for 2 h. Fused silica tubing was then statically coated at room temperature using 0.3 % (w/v) stationary phase solution in methylene chloride, that was filtered through a siantered glass filter. The thickness of the film was ca. 0.2 um. The column was then conditioned by heating from 40 to 280 ^{0}C at 2 ^{0}C/min. The column was then tested for its chromatographic performance using standard mixtures and environmental samples.

Results and discussion:

The molecular weight of the liquid crystalline polysiloxane obtained from monomer (#6) was ca. 15,582. The melting point of monomer was 120^{0}C, no transition temperature was observed using the capillary melting point method. However, LCP from this monomer melts at 80 ^{0}C and gives a clear isotropic state above 260 ^{0}C. It is always very difficult to find accurate transition temperatures but based on gas chromatographic properties of stationary phases transition temperatures can be predicted. Conversion of the monomer into poly siloxane was further confirmed by NMR spectra of both the monomer and polymer.

Chromatographic performance of the LCPS fused silica capillary column was investigated using different environmental samples and standards. GC-ECD traces of a PCDDs reference standard obtained on a LCPS column developed in this study and on a conventional DB-5 column are shown in Figure 2. The LCPS column shows better separation inspite of shorter column length. A comparable column efficiency was shown by the LCPS column to that of the DB-5 column.

We have already shown that the other type of liquid crystal column has superior selectivity for separation of 2,3,7,8-TCDD (14). The difficulty with that column was a very long retention time (ca. 100 min.) for elution of OCDD/OCDF (10). The LCPS developed in this study have comparable retention times to that of the DB-5 column in addition to better separation.

Comparison of separation of an Ontario fly ash extract on the LCPS and DB-5 column is shown in figure 3. It has been shown that a 60 m DB-5 column shows little separation of OCDD/OCDF (15). Similar separation is

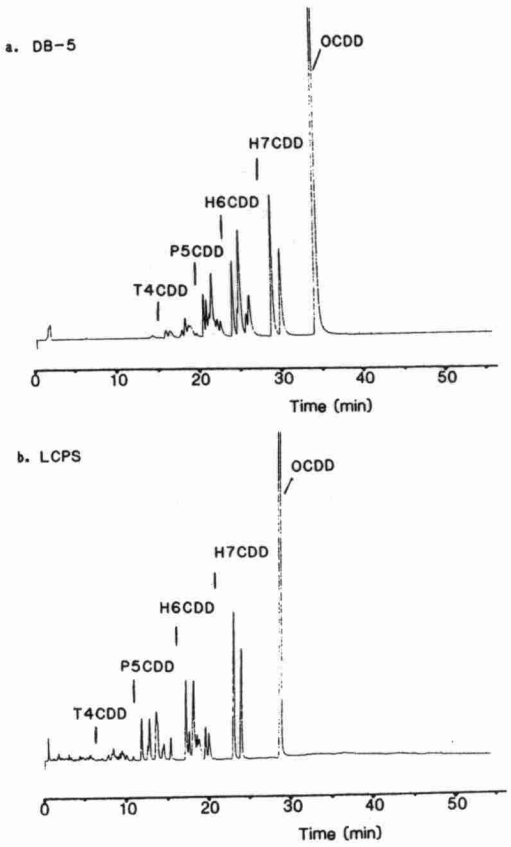


Figure 2.
GC-ECD traces of PCDD reference standard, a: column, DB-5, 30 m X 0.32 mm I. D. fused silica capillary, temperature program 80 ^{0}C for 1 min., programmed to 230 ^{0}C at 15 ^{0}C/min., programmed to 300 ^{0}C at 3 ^{0}C/min, b: column, Liquid crusalline polysiloxane, 20m X 0.32 mm I. D. fused silica capillary, temperature program 150 ^{0}C for 1 min., programmed to 250 ^{0}C at 3 ^{0}C/min.

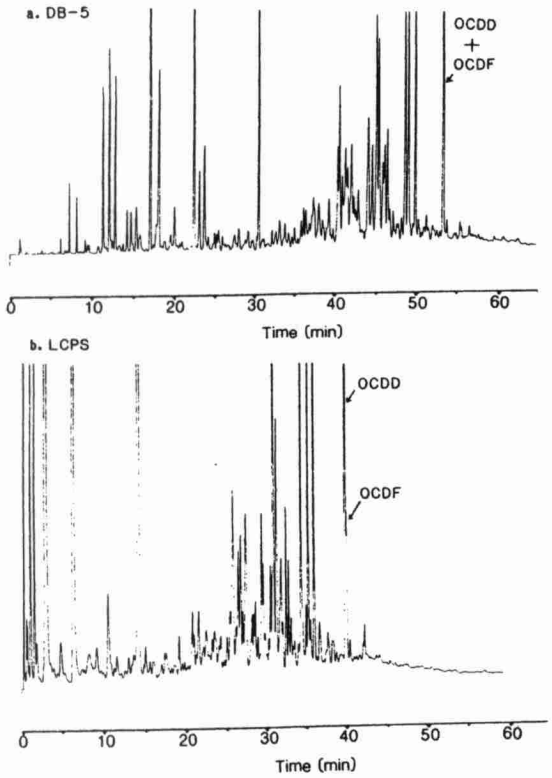


Figure 3.

GC-ECD traces of the Ontario Fly ash extrate, a: column, DB-5, 30 m X 0.32 mm I. D. fused silica capillary, temperature program 80 ^{0}C for 1 min., programmed to 230 ^{0}C at 15 ^{0}C/min., programmed to 300 ^{0}C at 3 ^{0}C/min,

b: column, Liquid crusalline polysiloxane, 20m X 0.32 mm I. D. fused silica capillary, temperature program 80 ^{0}C for 1 min., programmed to 200 ^{0}C at 5 ^{0}C/min, programmed to 250 ^{0}C at 2 ^{0}C.

achieved on the 20 m LCPS column developed in this study. It can be seen that OCDD/OCDF are not separated on a DB-5, 30 m long column.

To date, all LCPSs developed in this study have not been tested in detail as stationary phases, in particular, for isomer specific separation of 2,3,7,8-TCDD and TCDF using GC-MS/EISIM. However, those results will be included in the presentation.

References:

1. Janini, G. M.; Muschik, G. M., Zielinski, W. L. Jr.; Anal. Chem. 1978, 48, 809.
2. Zielinski, W. L. Jr., Miller, M. M., Ulma, G., Wasik, S. P.; Anal. Chem. 1986, 58, 2692.
3. Naikwadi, K. P., Rokushika, S., Hatano, H., Oshima, M.; J. Chromatogr. 1985, 331, 69.
4. Naikwadi, K. P., Jadhav, A. L., Rokushika, S., Hatano, H., Macromol. Chem. 1986, 187, 1407.
5. Rokushika, S., Naikwadi, K. P., Jadhav, A. L., Hatano, H.; HC&CC 1985, 8, 480.
6. Rokushika, S., Naikwadi, K.P., Jadhav, A. L., Hatano, H.; Chromatographia 1986, 22, 209.
7. Kuei, J. C., Tarbet, B. J., Jakson, W. P., Bradshow, J. S., Markedes, K. E., Lee, M. L.; 1985, 20, 303.
8 Apfel, M. A., Finkelmann, H., Janini, G. M, Laub, R. J., Luhmann, B. H., Price, A., Roberts, W. L., Show, T. J., Smith, C. A.; Anal. Chem. 1985, 57, 851.
9. Nishioka, M., Jones, B. A., Tarbet, B. J., Bradshow, J. S., Lee, M. L.; J. Chromatogr. 1986, 357, 79.
10. Naikwadi K. P., McGovern, A. M., Karasek, F. W.; Can. J. Chem. 1987, 65, 970.
11. Kong, R. C., Lee, M .L., Tominaga, Y., Pratap, R., Iwao, M., Castle R. N., Anal. Chem. 1982, 54, 1802.
12. Markides, K. E., Nishioka, M., Tarbet, B. J., Bradshaw, J. S., Lee, M. L.; Anal. Chem. 1985, 57, 1296.
13. Nishioka, M., Bradshaw, J. S., Lee, M. L., Tominaga, Y., Tedjamulia, M., Castal, R. N.; Anal. Chem. 1985, 57, 309.

14. Naikwadi, K. P., Karasek, F. W.;
J. Chromatogr.; 1986 361, 365.
15. Tong, H. Y., Shore, D. L., Karasek, F. W.;
Anal. Chem.; 1984, 56, 2442.

TD/5/T43
(8303)